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EUROPEAN PATENT APPLICATION

21 Application number: 87304790.6

51 Int. Cl. 4: **B 32 B 27/32**
B 32 B 27/18

22 Date of filing: 29.05.87

30 Priority: 30.05.86 GB 8613162

43 Date of publication of application:
02.12.87 Bulletin 87/49

84 Designated Contracting States:
BE DE ES FR GB IT

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54 Sealable films.

57 A sealable film having superior seal strength comprises a base layer comprising a polyolefin, e.g. polypropylene, and on one or both surfaces of the base layer 1 to 20 weight % of a mixture of 70 to 95 weight % of (a) a linear low density polyethylene or a polymer of at least one olefinically unsaturated monomer, at least one of which has a functional group, e.g. a copolymer of ethylene and vinyl acetate and (b) 50 to 30 weight % of a resin of molecular weight lower than that of the linear low density polyethylene or of the polymer, e.g. a hydrogenated petroleum resin.

EP 0 247 896 A1

Description

SEALABLE FILM

This invention relates to films based on polypropylene and which can be sealed by the application of heat.

Various polypropylene films have been described, e.g. in GB 2028168A, EP 002606, EP 135178 and DE 3247988 where the core or substrate of the film is polypropylene. Various additives can be added for example certain modulus improvers, certain anti-static media, siloxanes and pigments.

However, none of these documents teach that films may be obtained having a seal strength which is significantly improved compared with previously known polyolefin films. We have devised films having a seal layer needing only two components which show improved seal strength properties over those previously known having only two components in the seal layer, i.e. either the seal strength is much improved at the same temperature of sealing or the same seal strength can be obtained at lower temperatures.

According to this invention a sealable film comprises a base layer comprising a polyolefin said layer having on at least one surface thereof 1 to 20 weight % based on the weight of the base layer, of a film layer comprising a mixture of (a) 70 to 95, preferably 70 to 90 wt % of a linear low density polyethylene or a polymer of at least one olefinically unsaturated monomer provided at least one of the monomers has a functional group and (b) 5 to 30, preferably 10 to 30 wt % of a resin of molecular weight lower than that of the linear low density polyethylene (a) or of the polymer(a)

These films are capable of being used in the packaging industry and can meet the stringent criteria which are required for such films, such as sufficiently high modulus, inherent excellent clarity and in particular superior seal strength properties.

The base layer comprises a polyolefin. The polyolefin is preferably a polymer of a mono-alpha olefin containing from 2 to 8 carbon atoms and particularly 2 to 4 carbon atoms per molecule. Thus the polymer may be a homopolymer of one of the following olefins or a copolymer of two or more of the following olefins, ethylene, propylene, butene-1 and 4-methyl pentene-1. A particularly suitable material for the base layer of the film is polypropylene, especially a high molecular weight stereoregular predominantly crystalline polymer of propylene. Alternatively, a copolymer of propylene with up to 20 weight per cent of another olefin, e.g. ethylene, could be used. An especially preferred polyolefin is an isotactic polypropylene with a density of from 0.86 to 0.92 g/cc measured according to ASTM D1505 and a melt-flow index of from 1 to 15 g/10 min as determined according to ASTM DM 1238 (conditions 230°C and 2.16 kg). It may be made by Ziegler polymerisation methods using for example AlCl_3 and TiCl_4 as catalyst.

The base layer or core of the film has on one or preferably both surfaces 1 to 20 weight per cent, preferably 1 to 10 weight per cent and particularly

about 5 weight per cent for the or each surface based on the weight of the base layer, of film layer comprising a mixture of (a) 70 to 95, preferably 70 to 90 weight % of a linear low density polyethylene or the hereinbefore defined polymer and 5 to 30, preferably 10 to 30 weight per cent of (b) the low molecular weight resin, preferably a hydrogenated resin.

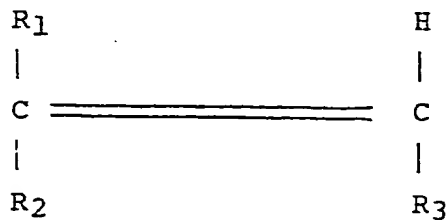
The linear low density polyethylene (LLDPE) is defined as a linear copolymer of ethylene and an alpha-olefin such as butene, hexene or octene or 4-methyl-pentene-1 having a density of between 0.875 and 0.939 gm/cc measured according to ASTM D 1505 and comprises at least 85 mole % of ethylene. It is usually prepared by polymerisation in the presence of Ziegler catalysts such as AlCl_3 and TiCl_4 .

One particular example of a linear low density polyethylene is very low density polyethylene (VLDPE). This is a linear copolymer of ethylene and an alpha-olefin such as butene, hexene or octene or 4-methyl pentene-1 having a density of from 0.875 to 0.915 g/cc measured according to ASTM D 1505 and comprises from 85 to 96 mol % of ethylene. It is also usually prepared by polymerisation in the presence of a Ziegler catalyst.

As an alternative to a linear low density polyethylene one can use a polymer of at least one olefinically unsaturated monomer, provided at least one of the monomers has a functional group. By functional group we mean a group containing at least one atom other than carbon or hydrogen, for example, the groups hydroxyl, carboxyl, carboxylic anhydride, carboxylate, ester, amino, amide, imide, halogen or sulphonate.

Suitable examples are an ethylene-vinyl acetate copolymer, polyvinyl chloride, polyvinylidene chloride, styrene-acrylonitrile copolymers and acrylonitrile-butadiene-styrene copolymers. Other polymers include random and graft copolymers where one of the monomers is ethylene or polar including acrylic acid, methacrylic acid, acrylate esters, maleic and other anhydrides and ionomeric materials formed by adding metal salts to such copolymers.

In general unsaturated monomers, copolymerizable with ethylene include unsaturated acids, acid anhydrides, and mono and diesters of the general formula:



wherein R_1 is hydrogen or methyl; R_2 is a OOCR_4 or -COOR_4 group wherein R_4 is hydrogen or a C_2 to

C₃₀, preferably a C₁ to C₄ straight or branched chain alkyl group and R₃ is hydrogen or -COOR₄. The monomer, when R₁ to R₃ are hydrogen and R₂ is -OOCR₄ includes vinyl alcohol esters of C₂ to C₁₇ monocarboxylic acids. Examples of such esters include vinyl acetate, vinyl isobutyrate, vinyl laurate, vinyl myristate, vinyl palmitate, etc. When R₂ is -COOR₄ such esters include C₈ Oxo alcohol acrylate, methyl acrylate, methyl methacrylate, lauryl acrylate, isobutyl methacrylate, palmityl alcohol ester of alpha-methylacrylic acid, C₁₃ Oxo alcohol esters of methacrylic acid, etc. Examples of monomers wherein R₁ is hydrogen and R₂ and R₃ are -OOCR₄ groups, include C₁₃ Oxo alcohol fumarate, di-C₁₃ Oxo alcohol fumarate, di-isopropyl maleate; di-lauryl fumarate; ethyl methyl fumarate, fumaric acid, maleic acid, etc.

Other unsaturated monomers copolymerizable with ethylene include C₃ to C₁₆ branched chain or straight-chain alpha monoolefins, as for example propylene, n-octene-1, 2-ethyldecene-1, n-decene-1, etc.

Small proportions, e.g. about 0 to 20 mole percent, of a third monomer, or even of a fourth monomer, can also be included in the copolymers, as for example a C₂ to C₁₆ branched or straight chain alpha monoolefin, e.g. propylene, n-octene-1, n-decene-1, etc. Thus, for example, a copolymer of 3 to 40 moles of ethylene with one mole of a mixture of 30 to 99 mole percent of unsaturated ester and 70 to 1 mole percent of olefin could be used.

The copolymers that are formed are random copolymers consisting primarily of an ethylene polymer backbone along which are distributed side chains of hydrocarbon or oxy-substituted hydrocarbon.

The Oxo alcohols used in preparing the esters mentioned above are isomeric mixtures of branched chain aliphatic primary alcohols prepared from olefins, such as polymers and copolymers of C₃ to C₄ monoolefins, reacted with carbon monoxide and hydrogen in the presence of a cobalt-containing catalyst such as cobalt carbonyl, at temperatures of about 300° to 400°F, under pressure of about 1,000 to 3,000 p.s.i., to form aldehydes. The resulting aldehyde product is then hydrogenated to form the Oxo alcohol, the latter being recovered by distillation from the hydrogenated product.

Particularly suitable examples include a copolymer of ethylene and a vinyl (or hydrocarbyl substituted) vinyl ester of a C₁ to C₃₀ monocarboxylic acid, preferably containing at least 89 wt % of ethylene (e.g. ethylene-vinyl acetate copolymer) such as ethylene-vinyl acetate copolymer containing 10 wt % vinyl acetate, an ethylene-vinyl acetate copolymer containing 95 wt % of ethylene, or one containing 0.10 to 1.95 wt % of the vinyl (or hydrocarbyl substituted vinyl) ester (e.g. vinyl acetate).

The other component of the surface layer(s) is a low molecular weight resin, preferably a hydrogenated resin. This resin has a molecular weight below that of the polyethylene or polymer and is usually less than 5000, preferably less than 1000, for example, 500 to 1000. The resin can be a natural or

synthetic resin and can have a softening point as mentioned by ASTM E-28 of from 60 to 180°C, eg 80 to 150°C preferably from 80 to 140°C.

Suitable resins which can be subsequently hydrogenated are hydrocarbon resins, ketone resins, polyamide resins, colophonium, coumarone resins, terpene resins, chlorinated aliphatic or aromatic hydrocarbon resins. Examples of hydrocarbon resins are polymers of coke oven gas, cracked naphtha, gasoil and terpene oil.

Particularly preferred hydrogenated resins are hydrogenated petroleum resins. These are usually prepared by catalytically hydrogenating a thermally polymerised steam cracked petroleum distillate fraction, especially a fraction having a boiling point of between 20°C and 280°C. These fractions usually are of compounds having one or more unsaturated cyclic rings in the molecule, such as cyclo dienes, cycloalkenes and indenenes. It is also possible to hydrogenate resins produced by catalytic polymerisation of unsaturated hydrocarbons.

Before hydrogenation occurs the polymerised resin is usually dissolved in a saturated hydrocarbon solvent such as heptane. The hydrogenation catalysts used may be nickel, reduced nickel, or molybdenum sulphide. Hydrogenation can take place in a single stage at a temperature of 200°C to 330°C, preferably from 210°C to 230°C at a pressure of 20 to 120 atmospheres, more preferably from 30 to 90 atmospheres for a period of 5 to 7 hours. After filtering off the catalyst, the solvent is removed by distillation and recovered for recycling. An improved hydrogenation process leading to increased yields of high quality hydrogenated hydrocarbon resins is described and claimed in European Patent 0082726 (Application No.82306853.1).

It is preferred that the or each outer film layer comprises 75 to 84.5 weight per cent of the linear low density polyethylene or defined polymer and 15.5 to 25 weight per cent of the low molecular weight resin, for example about 80 weight per cent of the polyethylene or polymer and about 20 weight per cent of the low molecular weight resin.

The films of this invention, i.e. multilayer films are suitably formed by combining the components (which may if desired include other components such as an antistatic medium, blocking agents and slip aids) of the base layer and surface layer(s) in a conventional manner, preferably by a simultaneous co-extrusion technique.

Multiple-layer films according to the invention may be unorientated or uniaxially orientated, but are preferably biaxially orientated by drawing in two mutually perpendicular directions in the plane of the film to impart strength thereto. Orientation of flat film may be effected by a stenter technique, while orientated tubular film is suitably produced by coextruding the polymeric materials in the form of a multi-layer tube from an annular die, cooling the extruded tube (the cast tube), reheating and inflating the tube by the so-called "bubble" process to introduce transverse orientation, and simultaneously elongating the tube longitudinally to orientate the film in a lengthwise direction. The film is then preferably "heat-set", i.e. dimensional stability of the

film is improved by heating the film, while restrained against thermal shrinkage, to a temperature above the glass transition temperature of the polymer from which the film is formed but below the melting point thereof.

The films may vary in thickness depending on the intended application, but films of a thickness of from 2 to 150 microns are usually suitable. Films intended for packaging are usually from 10 to 60 microns thick. The thickness of the or each layer is usually from 0.05 to 2.5 microns.

Example

In this Example co-extruded films of different composition were made and compared as to their sealability.

These films were biaxially orientated by drawing in two materially perpendicular directions in the plane of the film to impart strength thereto. The stenter technique was used to impart an orientation ratio of 500% in machine direction and of 900% in transverse direction. Each of the biaxially orientated films had two seal layers of 1 micron thickness while the total thickness was about 22 microns.

The first film which was for comparison purposes consisted of a core of isotactic polypropylene having a density of about 0.90 g/cc measured according to ASTM D 1505 and a melt flow index of 2.8 g/10 min as determined according to ASTM D1238 (conditions 230°C and 2.16 kg). On both faces of the core there was a copolymer of about 95.5 weight per cent propylene and 4.5 weight per cent of ethylene which was an isotactic copolymer with a density of 0.90 g/cc and a melt flow index of 6.5 g/10 min as determined according to ASTM D1238 (conditions 230°C and 2.16 kg).

The second film was the same as the first film except that on both faces of the core of isotactic polypropylene there was a film of LLDPE. LLDPE is linear low density polyethylene prepared by copolymerising ethylene with n-butene, using a Ziegler catalyst, the copolymer having at least 96 mol per cent ethylene and a density of 0.918 gm/cc.

The third film was the same as the first film except that each surface of the core was covered with a film comprising a blend of 80% by weight of LLDPE (see second film for details) and 20% by weight of a hydrogenated petroleum resin. The resin was prepared by catalytically hydrogenating a thermally polymerised steam cracked petroleum distillate fraction having a boiling point between 20°C and 280°C. The hydrogenation process was carried out as described in European Patent 0082726 (Application No. 82306853.1). The resulting resin was characterised by a Ring and Ball softening point of 125°C as measured by ASTM E 28.

The fourth film was the same as the third film except that each surface of the core was covered with a film comprising a blend of 80% by weight of VLDPE and 20% weight of the same hydrogenated petroleum resin as used in the manufacture of the second film. VLDPE is very low density polyethylene prepared by copolymerising ethylene with octene using a Ziegler catalyst, the copolymer having 95 mol per cent ethylene and a density of 0.911 g/cc

measured by ASTM D 1505 and a melt flow index of 7.0 g/10 min as determined according to ASDTM D1238 (conditions 190°C and 2.16 kg).

The accompanying Fig 1 and 2 show the results obtained for the seal strength and hot tack for films 1 and 2 (comparative), 3 and 4 (according to the invention).

These tests were carried out as follows:

Seal strength

This is the "cold" heat seal strength of the film which is measured after the seal has cooled to ambient temperature and the full potential strength of the seal has developed.

A Packforsk Hot Tack Tester (model 52-B) from Design & Test Consult AB (Bromma-Sweden) has been used to make the heat seals. A strip of 15 mm wide and some 280 mm long is thereto folded over upon itself and sealed together between the heated jaws of this instrument. The formed seal has an area of some 15 x 5 mm. Dwell conditions on the seal have been kept constant at a pressure of 5 bar and a dwell time of 0.5 seconds. To measure the seal strength, the instrument is used in a mode whereby upon opening of the sealing jaws the automatic peeling action used for hot tack measurements is not activated. The seal is instead cooled to ambient temperature. The unsealed ends of the strip are then attached to the jaws of a tensile testing machine. The force required to break the seal at a rate of 508 mm/min is recorded by the tensile tester and expressed as the seal strength in kg/15

Hot tack

This is the strength of the heat seal measured just after the seal has been made and before the thermal energy employed to form the heat seal has dissipated. The hot tack has been determined using the same Packforsk instrument. The heat seal is made as described above but just after the opening of the sealing jaws a peeling action is now automatically started and the force to break the seal is automatically recorded and expressed as the hot tack in kg/15mm. The peeling operation takes place at a controlled delay time (= time between opening of the jaws and start of the peeling operation) and controlled peel rate. Following constant conditions have been used for all hot tack determinations: delay time = 0.9 seconds, peel rate = 100 mm/s.

From Fig 1 it can be seen that the seal strength (kg/15 mm) for films 3 and 4 are much higher at temperatures of between 100° and 120° than for films 1 and 2.

From Fig 2 it can be seen that the hot tack (kg/15 mm) for film 3 is much better than for film 1 for temperatures up to about 130°C. For film 4 the hot tack is better than that of film 1 for temperatures up to about 110°C.

It is quite surprising that with the presence of the relatively small amount (20 weight %) of hydrogenated resin in the surface layer and using linear low density polyethylene one achieves such good results compared with the prior art film.

Claims

1. A sealable film comprising a base layer which comprises a polyolefin, said layer having on at least one surface thereof 1 to 20 weight % based on the weight of the base layer, of a film layer comprising a mixture of (a) 70 to 95 weight per cent of a linear low density polyethylene or a polymer of at least one olefinically unsaturated monomer provided at least one of the monomers has a functional group and (b) 5 to 30 weight per cent of a resin of molecular weight lower than that of the linear low density polyethylene or of the polymer.

2. A film according to claim 1 in which the film layer comprises a mixture of 70 to 90 wt % of the polymer as specified in claim 1 and 10 to 30 weight resin.

3. A film according to claim 1 or 2 wherein the polyolefin in the base layer is a polymer of a mono alpha olefin containing 2 to 4 carbon atoms per molecule, preferably polypropylene.

4. A film according to claim 3 wherein the polypropylene is a low pressure isotactic polypropylene with a density of from 0.86 to 0.92 g/cc measured by ASTM D 1505 and a melt flow index of from 1 to 15 g/100 min as determined according to ASTM D1238 (conditions 230°C and 2.16 kg).

5. A film according to any one of the preceding claims wherein the base layer has on each surface 1 to 10 weight per cent based on the weight of the base layer of said film layer comprising said mixture of linear low density polyethylene or defined polymer and low molecular weight resin.

6. A film according to any one of the preceding claims wherein the resin in the or each surface film layer is a hydrogenated resin, preferably a petroleum resin.

7. A film according to any one of the preceding claims wherein the resin has a softening point as mentioned in ASTM E-28 of 80 to 140°C.

8. A film according to any of claims 5 to 7 wherein the hydrogenated resin has been prepared by hydrogenating using a hydrogenation catalyst at a temperature of 200° to 330°C, a thermally polymerised steam cracked distillate fraction or a catalytically polymerised unsaturated hydrocarbon fraction.

9. A film according to any one of the preceding claims wherein the linear low density polyethylene is a linear copolymer of ethylene and an alpha-olefin having a density measured by ASTM D 1505 of from 0.875 to 0.939 gm/cc and comprising at least 85 mol %.

10. A film according to claim 9 in which the alpha-olefin is butene, hexene, octene or 4-methyl pentene-1.

11. A film according to claim 9 or claim 10 in which the density of the copolymer is 0.875 to

1.915 grams/cc and comprising from 85 to 96 mol % ethylene.

12. A film according to any one of claims 1 to 8 wherein the polymer of at least one olefinically unsaturated monomer is a copolymer of ethylene and a vinyl (or hydrocarbyl substituted) vinyl ester of a C₁ to C₃₀ monocarboxylic acid.

13. A film according to any one of the preceding claims wherein each surface film layer comprises 75 to 84.5 weight % of linear low density polyethylene or of defined polymer and 15.5 to 25 weight % of the low molecular weight resin.

14. A film according to any one of the preceding claims which is biaxially orientated.

15. A film according to any one of the preceding claims which is 10 to 60 microns thick and wherein the thickness of the or each outer film layer is 0.05 to 2.5 microns.

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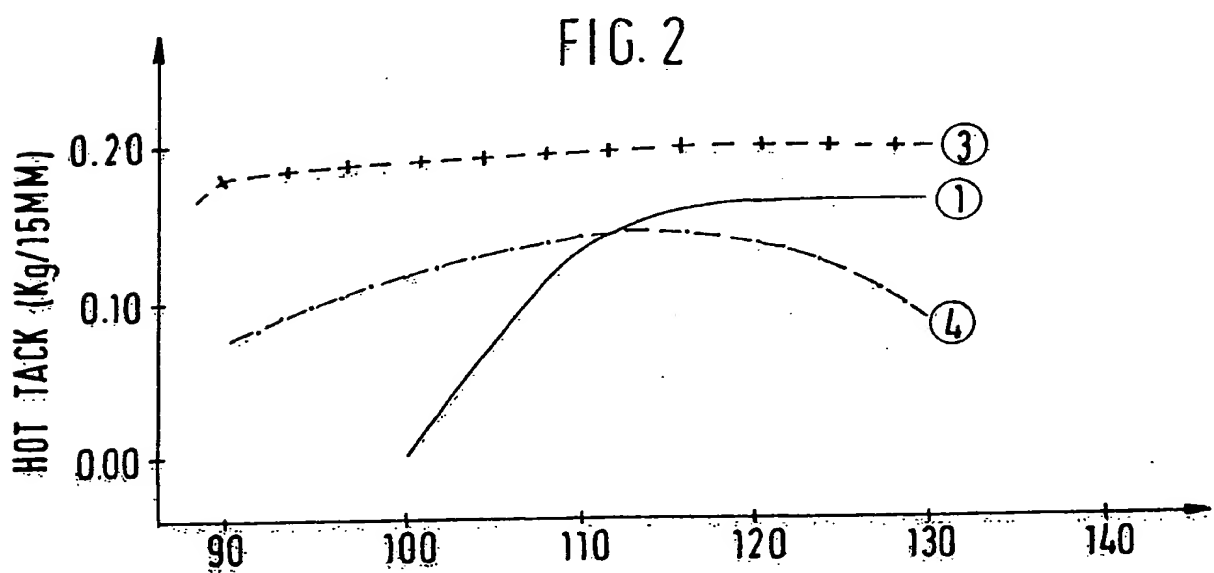
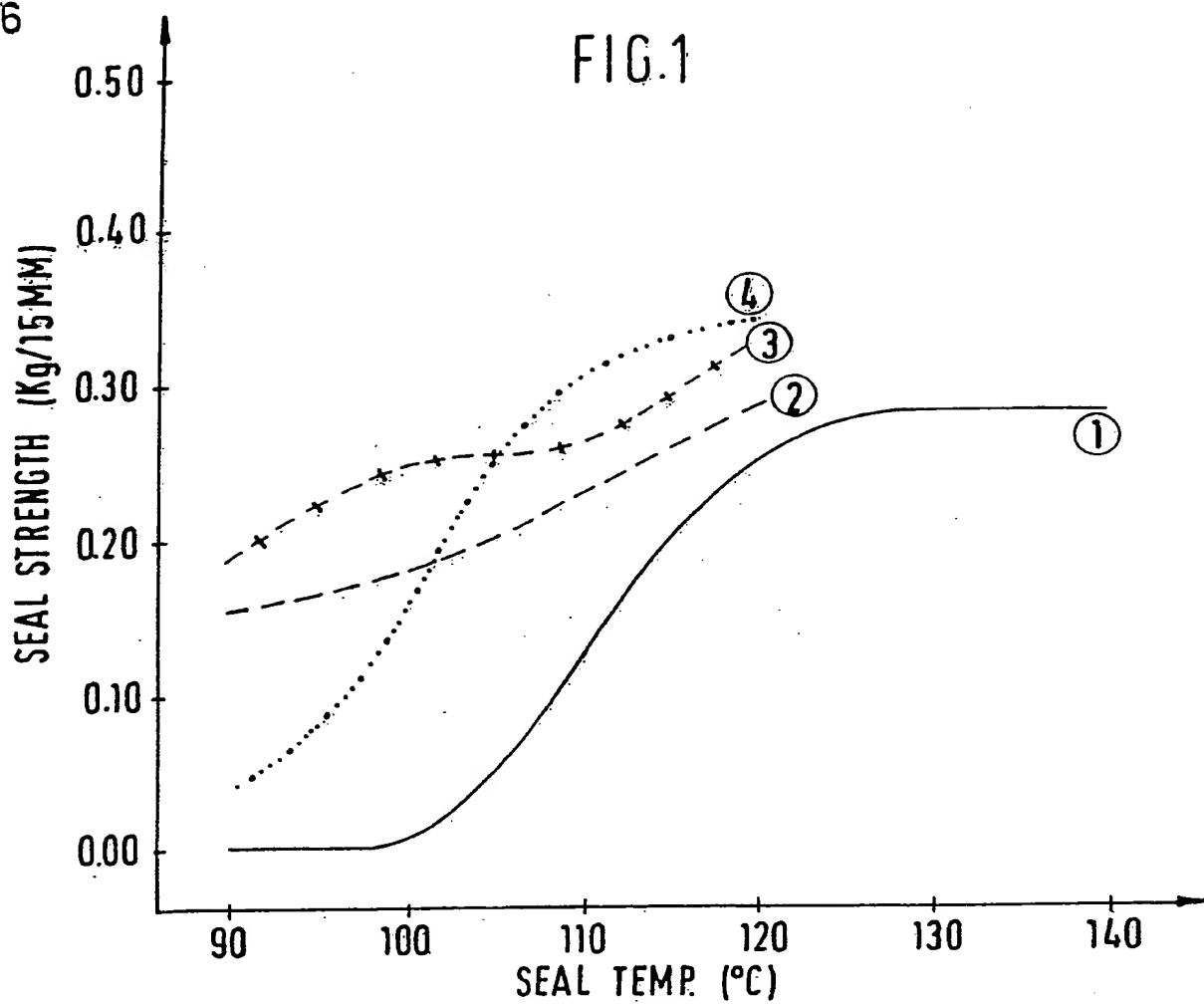
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DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
P, X	EP-A-0 201 798 (WOLFF WALSRÖDE AG) * Claims 1,3-8,10; page 2, line 11 - page 5, line 10; page 7, line 30 - page 8, line 7; examples 1-4 *	1-11, 13-15	B 32 B 27/32 B 32 B 27/18
A	--- EP-A-0 147 088 (MOBIL OIL) * Claims 1-3,5-8; page 2, alinéa 3 - page 5, alinéa 1; example 1 *	1-3,7, 9-11	
A	--- DE-A-3 015 056 (TOPPAN PRINTING CO.) * Claims 1-4; page 9, line 5 - page 11, line 18; page 15, lines 8-28; table II; example 2 *	1-3,8, 9,12	
			TECHNICAL FIELDS SEARCHED (Int. Cl.4)
			B 32 B
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 14-08-1987	Examiner BLASBAND I.
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	

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